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Electrical conductivity and dielectric properties of KH_2PO_4 crystals modified with KBr and NaBr

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Abstract : Pure KH_2PO_4 (KDP) and KDP crystals containing KBr and NaBr with/without gold doping were grown by slow evaporation technique All the grown crystals were γ- irradiated using ^{60}Co source Electrical conductivity measurements were carried out perpendicular to the unique direction before and after γ-irradiation The present measurement shows that the conductivity of KDP crystals increases with the addition of KBr and NaBr and with gold-doping as well as temperature. Computed values of activation energies from the conductivity measurements are given Dielectric constant is measured as a function of frequency Study confirms the contribution of space charge polarization

Keywords KDP crystals, dielectric constant, electrical conductivity, activation energy

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1. Introduction

Electrical conductivity of ionic crystals yields useful information regarding the mobility and production of lattice defects in these materials. In KH_2PO_4 type of crystals, the possible type of point defects which help the electrical conduction process are the ionization defects, *viz.* $(HPO_4)^{-2}$ and H_3PO_4 produced as a result of proton jump from one phosphate group to another along the same bond [1]. The electrical conduction in KDP crystals has been established to be protonic [2,3]. Earlier reports on KDP crystals doped with oxalate and chloride impurities have shown increase in conductivity, which has been explained as due to the replacement of $(H_2PO_4)^{-1}$ ions by $(C_2O_4)^{-2}$ and Cl^{-1} ions. [4,5]. It was also found that the activation energy for KDP crystals does not vary much on adding oxalate impurity of various concentrations [6]. It has been observed that the KDP system has become complex after ion irradiation [7] and it shows irregular behaviour with regard to conductivity property. At any temperature, the Gibb's free energy of a crystal is minimum when a certain fraction of ions leave the normal lattice. As the temperature increases, more and more defects are produced which in turn, increases the conductivity [8].

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We have made an attempt to modify KDP crystals by adding KBr and NaBr in definite ratios and doping with gold, with the aim of discovering new useful materials for academic and industrial use. Present paper reports the studies of electrical conductivity and dielectric constant of solution grown KDP crystals containing KBr and NaBr with/without gold doping.

2. Experimental

2.1. Crystal growth and testing :

Single crystals were grown from aqueous solution by slow evaporation technique at room temperature using AR grade KDP, KBr and NaBr compounds. KDP was added with KBr and NaBr separately, each in three different molecular ratios, *viz.* KDP: *X* (*X* = KBr or NaBr) 10:0.0 (pure KDP), 9:1 and 8:2.

Au^+-doped crystals were grown by adding a definite volume of tetra-auro chloric acid solution to the mixture of KDP containing KBr or NaBr.

Grown crystals were found to be transparent and exhibited scalenohedral (twelve sided polyhedron) morphology. Some large size crystals with high transparency and defect-free, were used for electrical conductivity and dielectric measurements.

The KDP crystals modified with KBr and NaBr, were analysed by XRD pattern and energy dispersive X-ray spectroscopy (EDAX) to check the presence of doped elements. Figures 1 and 2 indicate that the impurities have entered into the lattice of the KDP crystals.

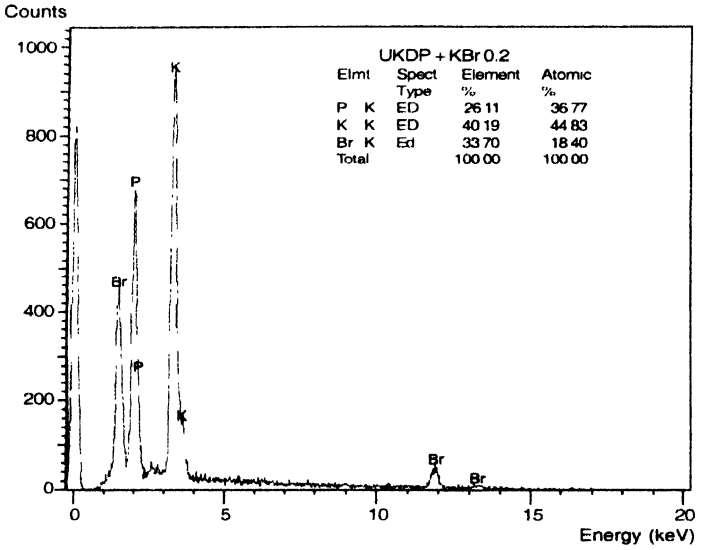

Figure 1. EDAX data of $(KDP)_{0.8}$ $(KBr)_{0.2}$ crystals.

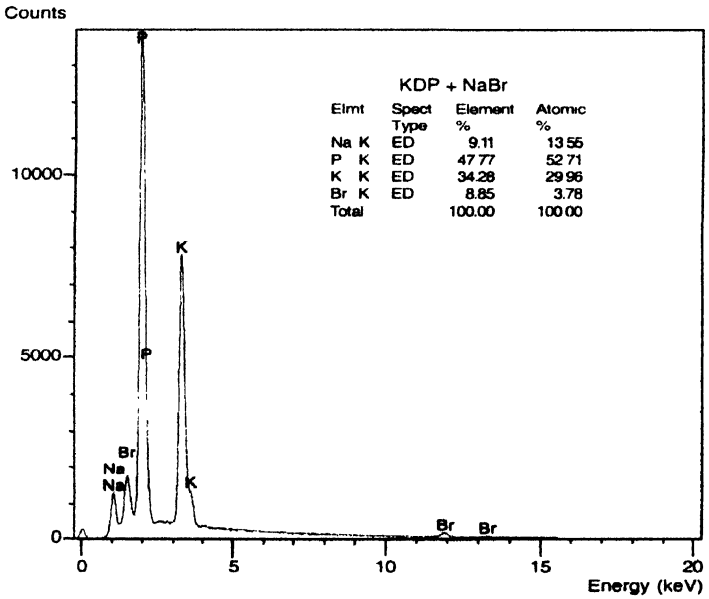

Figure 2. EDAX data of $(KDP)_{0.8}$ $(NaBr)_{0.2}$ crystals.

2.2. Dielectric measurement:

Some polished crystals of required sizes were electroded on both sides with air-drying silver paste for capacitance measurement. A Multi-frequency LCR meter (HP 4275A) was used to measure capacitance (C) and dissipation factor (D) of the crystals as a function of frequency at room temperature. The dielectric constant (ε) and dielectric loss ($\tan\delta$) were obtained from C and D.

2.3. Conductivity measurement :

Both undoped and Au^+-doped KDP crystals were subjected to γ-irradiation using ^{60}Co source to a dosage of 5 Mrads. The conductivity measurement was carried out for both irradiated and non-irradiated crystals along a-direction (perpendicular to the unique axis) using the conventional two-probe technique at various temperatures in the range from room temperature to 150°C. The conductivity values were fitted into the equation $\sigma(T) = \sigma_0 \exp(-E/kT)$, where k is the Boltzmann's constant, T is the absolute temperature, σ_0 is a constant which depends on the material and E is the activation energy.

3. Results and discussion

(i). The variation of dielectric constant (ε) and dielectric loss ($\tan\delta$) at room temperature for KDP, Au^+-doped KDP and KDP containing KBr and NaBr with and without gold doping are shown in Figures 3-6. It is observed that the dielectric constant

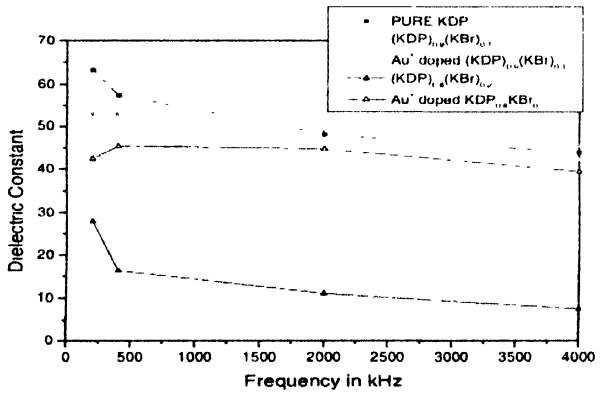

Figure 3. Variation of dielectric constant with frequency in KDP crystals containing KBr with and without Au^+-doping

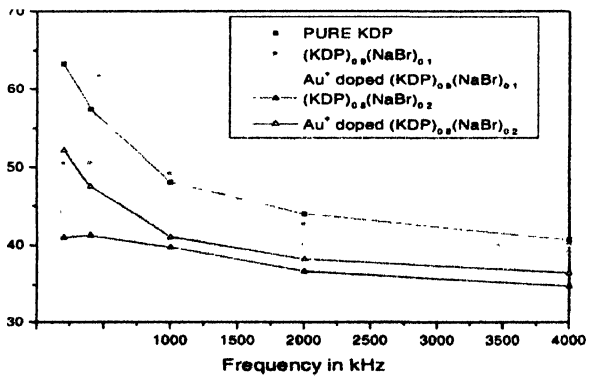

Figure 4. Variation of dielectric constant with Frequency in KDP crystals containing NaBr with and without Au^+-doping.

(ε) decreases with the increase in the frequency. Values of dielectric constant and dielectric loss at 100 kHz and 1 MHz frequency for pure KDP, Au^+-doped KDP and KDP crystals containing KBr and NaBr with and without gold-doping are given in Table 1. The dielectric constant of a material is generally due to the contributions from ionic, electronic, orientational and space charge polarizations. At low frequencies, all polarizabilities are operative, hence ε is high. As frequency increases, one polarization mechanism after another is frozen out. The first to stop contribution to ε is orientational component, then the ionic and lastly the electronic [9, 10].

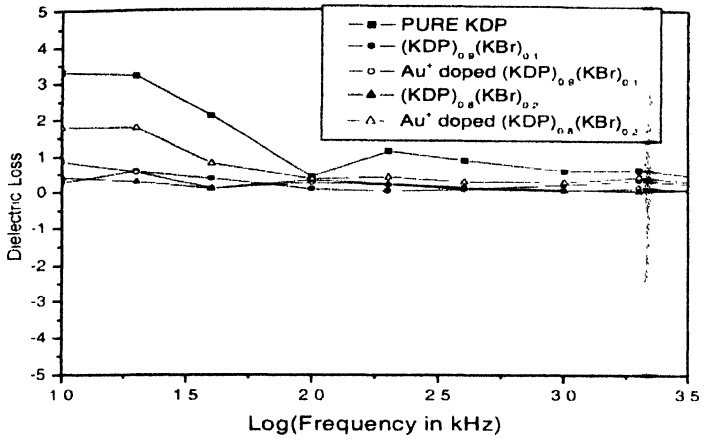

Figure 5. Variation of dielectric loss with Log(frequency) in KDP crystals containing KBr with and without Au^+-doping

The dielectric loss ($\tan\delta$) is due to the resistive component that makes them lossy, so that they dissipate some of the applied ac energy. $\tan\delta$ in the present study was found initially to decrease with frequency and later almost a constant over a range of frequency.

(ii) The σ values obtained along the a-direction are within the experimental error. Figures 7-11 show the plots of $\log\sigma$ (T) *versus* 1000/T for the pure and KBr and NaBr added KDP crystals with and without gold-doping before and after γ-irradiation when the field is applied along the *a*-direction. The computed values of the activation energy E for pure and impurity added crystals, are given in Table 2. It can be seen from the figures that the electrical conductivity is increased with addition of KBr and

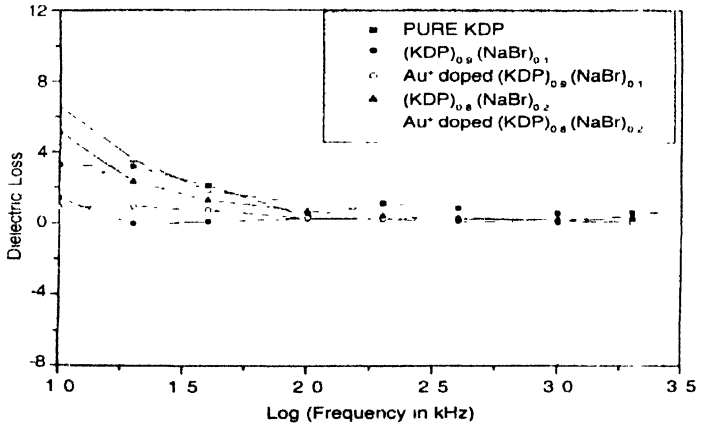

Figure 6. Variation of dielectric loss with Log (frequency) in KDP crystals containing NaBr with and without Au^+-doping.

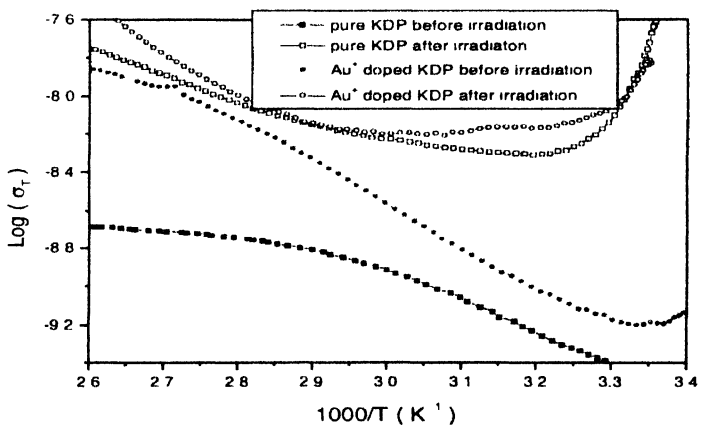

Figure 7. Variation of $\text{Log}(\sigma_T)$ with 1000/T in KDP and Au^+-doped crystals before and after irradiation.

Table 1. Values of dielectric constant (ε) and dielectric loss ($\tan\delta$) of pure and impurity KDP crystals

Sample	KDP crystals added with 10 mole% of alkali halides				KDP crystals added with 20 mole% of alkali halides			
	At 100 kHz		At 1 MHz		At 100 kHz		At 1 MHz	
	ε	$\tan\delta$	ε	$\tan\delta$	ε	$\tan\delta$	ε	$\tan\delta$
Pure KDP	57.38	0.4246	40.689	0 5981	---	---	---	---
Au^+-doped KDP	54.42	1 3006	36.07	0.2669	---	---	---	---
KDP+KBr	45.44	0 0591	40.24	0.1851	36 38	0 7242	35 09	0.3228
Au^+-doped KDP+KBr	42 21	0.2491	35.63	0 2850	39.40	0 3586	33.11	0 2748
KDP+NaBr	42.66	0.2944	36.25	0.0688	36.63	0.7143	32.12	0.2731
Au^+-doped KDP+NaBr	40.79	0.3304	39 97	0 2078	41 07	1.1581	34.74	0.2362

NaBr and with irradiation. The conductivity graphs exhibit the usual intrinsic and extrinsic regions. Conduction at high temperature is the intrinsic conduction region, which is due to the thermally created vacancies as well as the variation of their mobility with temperature. The low activation energy suggests that oxygen vacancies are responsible for conduction in this region. Extrinsic region *i.e.* the low temperature region is structure-sensitive region. Hence, the addition of impurities further increases the electrical conductivity in the extrinsic region

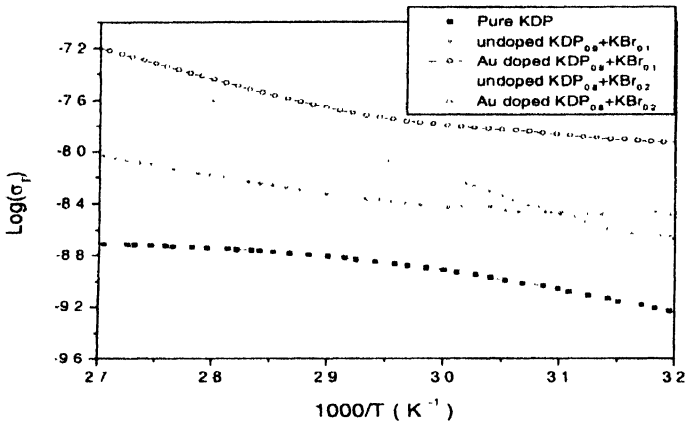

Figure 8. Variation of Log(σ_T) with 1000/T in KDP crystals containing KBr with and without Au^+-doping

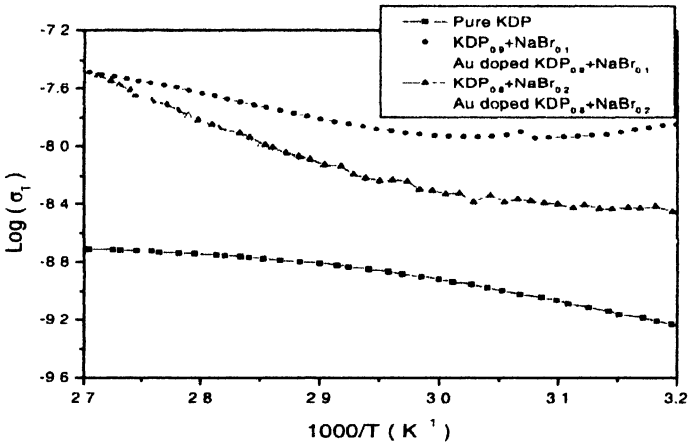

Figure 9. Variation of Log(σ_T) with 1000/T in KDP crystals containing NaBr with and without Au^+-doping.

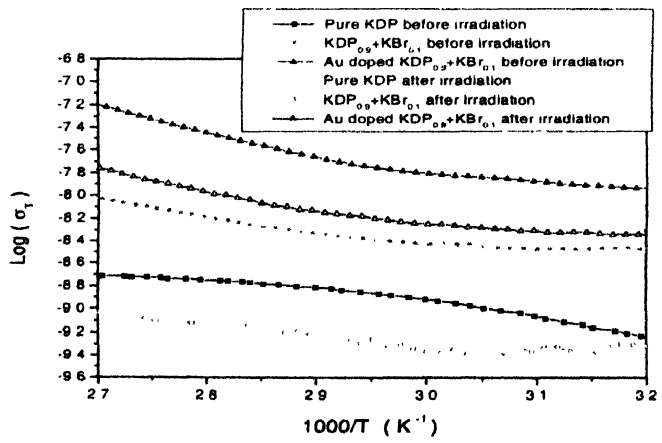

Figure 10. Variation of Log(σ_T) with 1000/T in KDP crystals containing KBr with and without Au^+-doping before and after irradiation.

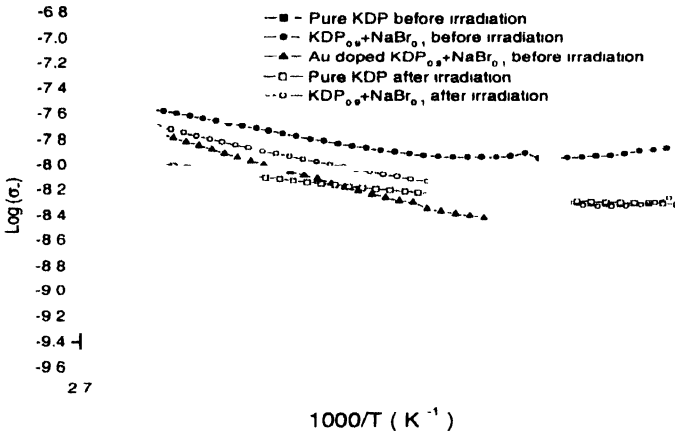

Figure 11. Variation of Log (σ_T) with 1000/T in KDP crystals containing NaBr with and without Au^+-doping before and after irradiation

Table 2. Values of activation energy (E) in eV of pure and impurity added KDP crystals.

Sample	KDP crystals added with 10 mole% of alkali halides before irradiation	KDP crystals added with 20 mole% of alkali halides before irradiation	KDP crystals added with 10 mole % of alkali halides after irradiation
Pure KDP	0 3076		0 2309
Au+-doped KDP	0 4368		0 4481
KDP + KBr	0 3223	0 3785	0.5704
Au+-doped KDP + KBr	0.4576	0.5710	0 3666
KDP + NaBr	0.3610	0.5580	0 3882
Au+-doped KDP + NaBr	0 4390	0.6029	- --

Accuracy = ±0.0001 ev

Conductivity obtained in the present study, is in good agreement with that obtained by previous authors for the KDP crystals [4-6,11].

The electrical conduction in dielectrics is mainly a defect-controlled process in the low temperature region (structure sensitive region). The defect concentration will increase exponentially with temperature and consequently the electrical conduction also increases. The addition of impurity further increases the electrical conduction in the temperature region

onsidered. For the concentrations of the impurities studied, he electrical conductivity increases with increase in the impurity ontent of the crystal.

In the case of KH_2PO_4, the most important contribution to n understanding of the structure is given by West [7]. The tomic arrangements are such that each P atom is surrounded by four O atoms at the corners of a regular tetrahedron. Each $_4$ group is linked with four other PO_4 groups by H-bonds The upper O of one PO_4 group is linked with the lower oxygen of the neighboring PO_4 group by an H-bond. Neutron diffraction studies revealed that each PO_4 group has two nearest H atoms and as a group they form (H_2PO_4) ions. The PO_4 group and the K ions are built-up in such a way that K and P atoms alternate each other at a distance of $c/2$ along the c-axis. Each K is surrounded by eight O's and four of them are nearer than the other four.

For electrical conduction, it is proved that K ion does not ontribute much [4, 6]. The conduction is mainly due to the nions namely (H_2PO_4) ions. The H-bond with the PO_4 group is n such a way that one H-bond is associated with the upper O nd the other H-bonds with lower O. This arrangement gives a avourable picture of conduction mechanism.

As the temperature is increased, the spontaneous olarization decreases and becomes zero at and above the Curie emperature (123K). This variation is due to the change in the onfiguration of the PO_4 group. The H-bonds which are ssociated with either the upper two oxygen atoms or lower two xygen atoms before the transition temperature, change their onfiguration in such a way that one H-bond is associated with ne of the upper O atoms and the other with one of the lower O toms. This type of transformation of H-bonds is called M defect. n a real crystal, the presence of M defect creates an H-bond vith two hydrogen atoms at one end and other H-bond with no ydrogen at the other end. These defects are known as D and L lefects respectively. O'Keeffe and Perrino [2] introduced another ype of defect $(HPO_4)^-$ and $(H_3PO_4)^+$ formed by self-ionization f H_2PO_4. These charges combine with H_2PO_4, giving rise to an I defect. This M defect in turn by intra bond jump, annihilates tself and yields L and D pairs. These defects are responsible for he electrical conduction in KH_2PO_4 crystals.

The increase in conductivity of KDP crystals containing KBr or NaBr impurities can be explained by considering the eplacement of $(H_2PO_4)^{-1}$ ions by Br^- ions. This is in agreement vith the results obtained by the previous workers in the case of loped KDP crystals [4, 11, 12].

Computed values of activation energy (E) from the plots of σ (T) *versus* 1000/T confirm higher values of activation energy in case of KDP crystals containing NaBr or KBr and also with Au^+-doping. Irradiated crystals have answered for still higher activation energies. This increase in activation energy gives a clue regarding the diffusion of impurities to the regular position, hence the increase in E.

4. Conclusions

Pure and NaBr and KBr modified KDP single crystals with and without gold-doping were grown by slow evaporation technique. EDAX data confirms that the impurities have gone into the lattice of the crystal. Electrical conductivity was measured along the a-direction at various temperatures ranging from room temperature to 150 °C. The present study gives further evidence that the conduction in KDP is mainly due to the anions and not due to the cations. The present study indicates that the conductivity increases with the addition of KBr and NaBr and also with gold-doping. The further increase in conductivity is due to the effect of radiation-induced defects. Higher value of activation energy in case of KDP crystals containing NaBr and KBr, also with Au^+-doping gives a clue regarding the diffusion of defects either to the regular position or to the interstitial position.

References

[1] A W George *Nucl Instrum Meth Phys Res* **B39** 708 (1989)

[2] M O'Keeffe and C T Perrino *J Phys Chem Solids* **28** 211 (1967)

[3] M Shanmugham, F D Gnanam and P Ramasamy *Indian J Pure Appl. Phys* **20** 579 (1982)

[4] M Shanmugham, F D Gnanam and P Ramasamy *Indian J Pure Appl Phys* **23** 82 (1985)

[5] P S Ramasubramanian and C Mahadevan *Indian. J. Pure Appl. Phy.* **29** 285 (1991)

[6] K S Udupa, P Mohan Rao, Aithal Sriramana, A P Bhat and D K Avasthi *Bull. Mater. Sci.* **20** 1069 (1997)

[7] J West *Z. Krist (Germany)* **74** 306 (1930)

[8] S C Jain and S L Dahake *Indian J. Pure Appl. Phys.* **2** 71 (1964)

[9] P Suryanarayana, H N Acharya and K Rao *J. Mater. Sci Lett.* **3** 21 (1984)

[10] S Sankara Narayanan Potty and M Abdul Khadhar *Bull Mater. Sci* **23** 361 (2002)

[11] L B Harris and G J Vella *J. Appl. Chem.* **17** 151 (1966)

[12] J Albin Sancta, A Gnana Sutha, T H Freeda, C Mahadevan and C Balasingh *Indian. J. Phys.* **75A** 245 (2001)